(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 439 316 B1**

(12) # EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **02.11.95** (51) Int. Cl.[6]: **C11D 1/14**, C11D 1/83

(21) Application number: **91300456.0**

(22) Date of filing: **21.01.91**

(54) **Detergent composition.**

(30) Priority: **22.01.90 GB 9001404**

(43) Date of publication of application:
31.07.91 Bulletin 91/31

(45) Publication of the grant of the patent:
02.11.95 Bulletin 95/44

(84) Designated Contracting States:
CH DE ES FR GB IT LI NL SE

(56) References cited:
EP-A- 0 342 917
GB-A- 1 257 679
US-A- 3 480 556

DATABASE WPIL Derwent Publications Ltd., London, GB; DATABASE WPI, accession no. 72-40688T, week 25; & JP- A - 47021232 (NISSAN)

(73) Proprietor: **UNILEVER PLC**
Unilever House
Blackfriars
London EC4P 4BQ (GB)
(84) Designated Contracting States:
GB

(73) Proprietor: **UNILEVER N.V.**
Weena 455
NL-3013 AL Rotterdam (NL)
(84) Designated Contracting States:
CH DE ES FR IT LI NL SE

(72) Inventor: **Smith, Bryan Cecil**
Mozartlaan 46
NL-3055 KL Rotterdam (NL)
Inventor: **Falou, Mohamed Sami**
19 Motcombe Farm Road
Heald Green,
Cheadle,
Cheshire SK8 3RW (GB)
Inventor: **Hull, Michael**
Windcliffe,
Alcanley Road
Helsby,
Wirral WA6 9PS (GB)
Inventor: **Giles, Dennis**
33 Brookhurst Road
Bromborough
Wirral,
Merseyside L63 EH (GB)

EP 0 439 316 B1

(74) Representative: **Fransella, Mary Evelyn et al**
Unilever PLC
Patent Division
Colworth House
Sharnbrook
Bedford MK44 1LQ (GB)

Description

This invention relates to a detergent composition, in particular to a detergent composition for washing fabrics.

Fabric washing compositions contain, as an essential ingredient, a surfactant system whose role is to assist in the removal of soil from the fabric and its suspension in the wash liquor. Suitable detergent active materials fall into a number of classes, including anionic, nonionic and cationic materials and marketed products contain materials selected from one or more of these classes.

The most widely used anionic detergent active materials are the alkyl benzene sulphonates and these provide satisfactory results especially at high temperatures. There has been a desire to find alternative anionic surfactants for use in circumstances when alkyl benzene sulphonates are undesirable, but generally speaking the performance of other anionic detergent active materials is unsatisfactory.

Among such alternative anionic surfactants are the primary alcohol sulphates (PAS) otherwise known as alkyl sulphates. PAS may be derived from both synthetic and natural alcohols containing from about 8 to 18 carbon atoms. Examples of suitable alcohols which can be used in alkyl sulphate manufacture include decyl, lauryl, myristyl, palmityl and stearyl alcohols and the mixture of fatty alcohols derived by reducing the glycerides of tallow and coconut oil. Natural alcohols, for example tallow or coconut alcohol, give rise to straight chain, or linear, PAS. Synthetic alcohols for example those produced by the Oxo process can give rise to straight or branched chain PAS.

In the past PAS derived from tallow fat that is to say linear PAS has been recommended for use in fabric washing compositions. Thus, GB 1 399 966 (The Procter and Gamble Company) discloses a detergent composition in which the surfactant system is a mixture of sodium tallow alkyl sulphate and a nonionic detergent active material. However, tallow PAS suffers from the disadvantage that its performance at low temperatures is poor. With the trend towards lower wash temperatures this becomes a serious disadvantage.

GB 1 399 966 referred to above also discloses the possibility of using the PAS derived from coconut oil, also linear. The performance of tallow PAS at low temperatures is poor.

The consumer expects a single product to perform satisfactorily both at high and low temperatures, neither tallow PAS nor coconut PAS can achieve this.

In our patent application EP 342 917A it is suggested that a PAS which has a wider spread of chain lengths than is derivable from either tallow or coconut alcohol can perform better than tallow PAS at low temperatures and better than coconut PAS at higher temperatures. The PAS disclosed in EP 342 917A are derived from either synthetic or natural alcohols but are all linear PAS.

US 3 480 556 (Atlantic Richfield) discloses C_1/C_2 branched (preferably methyl- or ethyl- branched) PAS in a formulation for dishwashing. JP 47 021 232B (Nissan) discloses a detergency negative for the replacement of C_{11} linear PAS with branched PAS of unspecified branching.

We have now found that there are benefits in performance particularly in the removal of oily soil when certain specific branched PAS materials are used, especially when they are combined with certain types of nonionic surfactant. These benefits can be seen over a range of temperatures.

Thus according to a first aspect of the present invention there is provided a detergent composition for washing fabrics, the composition containing a surfactant system comprising an anionic surfactant the major ingredient of which is a primary alkyl sulphate with primary alkyl chain length between 10 and 20 carbon atoms, wherein more that 10% by weight of the total primary alkyl sulphate is branched, and more than 5% by weight of the total primary alkyl sulphate comprises material wherein the branches contain at least 4 carbon atoms.

In compositions of this invention, the branched PAS preferably contains between 15% and 70% by weight of branching, and most preferably between 30% and 65% of branching, based on the total weight of PAS.

It is preferred to use branched PAS having a range of primary alkyl chain lengths for example between 12 and 18 carbon atoms, or between 12 and 16 carbon atoms, most preferably between 13 and 15 carbon atoms.

The water soluble salts of these anionic surfactants are preferred, especially the alkali metal salts thereof.

Preferred compositions according to the invention include from 2% to 50%, such as from 4% to 30% by weight of the surfactant system.

In addition to the branched PAS materials according to the invention, other PAS materials may be included in the composition, for example linear PAS.

The compositions of the invention also preferably contain a nonionic surfactant. We have found it to be of advantage if such a nonionic surfactant has an HLB of less than 10.5, preferably less than 10.

Suitable nonionic surfactants which may be used are the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C_6-C_{22}) phenols-ethylene oxide condensates, the condensation products of aliphatic (C_8-C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine.

When alkylene oxide adducts of fatty materials are used as the nonionic surfactants, the number of alkylene oxide groups per molecule has a considerable effect upon the HLB of the nonionic surfactant. The chain length and nature of the fatty material is also influential, and thus the preferred number of alkylene oxide groups per molecule depends upon the nature and chain length of the fatty material.

We have found it of advantage that the weight ratio between the anionic surfactant and the nonionic surfactant lies between 10:1 and 1:4, most preferably between 4:1 and 1:3.

The surfactant system may include other surfactant materials in addition to the specified alkyl sulphate and the above mentioned nonionic materials. These other surfactant materials may be selected from other anionic detergent active materials, zwitterionic or amphoteric detergent active materials or mixture thereof.

Any such further surfactant materials should preferably be present at a level which is no more than 25% preferably not more than 10% of the total amount of surfactant in the composition.

The other anionic detergent active materials may be the usual water-soluble alkali metal salts of organic sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl (C_9-C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10}-C_{15}) benzene sulphonate; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and sulphonates; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_8-C_{20}) with sodium bisulphite and those derived from reacting paraffins with SO_2 and Cl_2 and then hydrolysing with a base to produce a random sulphate.

The compositions of the invention may contain a detergency builder material, this may be any material capable of reducing the level of free calcium ions in the wash liquor and will preferably provide the compositions with other beneficial properties such as the generation of an alkaline pH and the suspension of soil removed from the fabric. The amount of builder material in a composition of this invention may in particular be from 15% to 60% by weight of the composition.

Examples of phosphorous-containing inorganic detergency builders, when present, include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates, metaphosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, orthophosphates and hexamataphosphates.

Examples of non-phosphorous-containing inorganic detergency builders, when present, include water-soluble alkali metal carbonates, bicarbonates, silicates and crystalline and amorphous aluminisilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate (with or without calcite seeds), sodium and potassium bicarbonates and silicates.

Examples of organic detergency builders, when present, include the alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetyl carboxylates and polyhydroxysulphonates. Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids and citric acid.

It is preferred that the compositions according to the invention be alkaline, that is at the concentration of 1 g/l in distilled water at 25 °C the pH should be at least 8, preferably at least 10. To this end the compositions may include a water-soluble alkaline salt. This salt may be a detergency builder or a non-building alkaline material.

Apart from the ingredients already mentioned, a number of optional ingredients may also be present.

Examples of other ingredients which may be present in the composition include fabric softening agents such as fatty amines, fabric softening clay materials, lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids, lather depressants, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, peracid bleach

precursors, chlorine-releasing bleaching agents such as tricloroisocyanuric acid, inorganic salts such as sodium sulphate, and; usually present in very minor amounts, fluorescent agents, perfumes including deodorant perfumes, enzymes such as proteases, cellulases and amylases, lipases germicides and colourants.

Although detergent compositions generally include sodium sulphate it may sometimes be desirable to have compositions which are sulphate free or contain low levels of sulphate.

The detergent compositions according to the invention may be prepared by a number of different methods according to their physical form. In the case of granular products they may be prepared by dry-mixing or coagglomeration. A preferred physical form is a granule incorporating a detergency builder salt and this is most conveniently manufactured by spray-drying at least part of the composition. In this process a slurry is prepared containing the heat-insensitive components of the composition such as the surfactant system, builder material and filler. The slurry is spray-dried to form base powder granules with which any solid heat-sensitive ingredients may be mixed, such ingredients including bleaches and enzymes. The specified nonionic surfactants can be liquidified by melting or solvent dissolution and sprayed onto the base powder granules, rather than including them in the slurry for spray-drying. The invention will now be described in more detail in the following examples.

Examples 1 to 4

Wash liquors were prepared in water having a hardness of 24°FH (equivalent to a free calcium ion concentration of 2.4 x 10^{-3} molar). The wash liquor contained the equivalent of 6g/l of a composition containing (by weight)

	1	2	3	4
Coconut PAS (ELFAN 280)	6	-	-	-
SYNPROL SULPHATE	-	6	-	-
DOBANOL 45 SULPHATE	-	-	6	-
LIAL 145 SULPHATE	-	-	-	6
SYNPERONIC A7	2	2	2	2
SYNPERONIC A3	5	5	5	5
Zeolite	24	24	24	24
SOKALAN CP5	4	4	4	4
Soluble "C" silicate	0.8	0.8	0.8	0.8
Sodium carbonate	10	10	10	10
Sodium sulphate	20	20	20	20
Sodium metaborate	11	11	11	11

The sodium metaborate was included as being equivalent in ionic strength to 8% sodium perborate monohydrate which would be present in practice. The bleach is left out of these experiments to avoid confusion between detergency and bleaching effects in the interpretation of the results. The anionic surfactants used were as set out in the following table:

Example No.	Anionic	% branching	% branching (4 or greater)	Chain Length (atoms)
1	ELFAN 280	none	none	(12/14/16/18)
2	SYNPROL SULPHATE	46	2.3	(13/15)
3	DOBANOL 45 SULPHATE	18	8.8	14/15
4	LIAL 145 SULPHATE	61	30	14/15
ELFAN 280 is ex Akzo, SYNPROL SULPHATE is ex ICI, DOBANOL 45 SULPHATE is the sulphate of DOBANOL 45 alcohol ex Shell, LIAL 145 SULPHATE is the sulphate of LIAL 145 alcohol ex Enichem.				

In examples 1 to 4 the nonionic surfactant was SYNPERONIC A7 (ex ICI) which is principally C_{13}/C_{15} alcohol ethoxylated with an average of 7 moles of ethylene oxide mixed with SYNPERONIC A3 (ex ICI) which is principally $C_{13}/_{15}$ alcohol ethoxylated with an average of 3 moles of ethylene oxide. This mixture has an HLB of approximately 9.

The wash liquors were used to wash a fabric load at liquor to cloth ratio of 50:1. The load included a number of polyester monitors to which had previously been applied an amount of H^3 tagged triolein. Measurement of the level of tagged triolein after washing, using standard radio-tracer techniques, gives an indication of the degree of detergency, i.e. soil removal, obtained.

The wash time was 20 minutes with an agitation of 70 rpm. Washes were isothermal at 40 ° C.

The results obtained were as follows:

Example No.	Anionic	Branched ?	% soil removal
1	ELFAN 280	No	21.4
2	SYNPROL SULPHATE	Yes	23.3
3	DOBANOL 45 SULPHATE	Yes	27.6
4	LIAL 145 SULPHATE	Yes	28.6

From these results it is apparent that the branched chain PAS outperforms the linear chain PAS.

Examples 5 to 7

Experiments were conducted in a similar manner to Examples 1 to 4 excepting that the wash temperature was 30 ° C and the water used was 25 ° FH (equivalent to 2.5 x 10^{-3} mol/l of calcium).

	Example		
	5	6	7
ELFAN 280	9	-	-
SYNPROL SULPHATE	-	9	-
DOBANOL 45 SULPHATE	-	-	9
SYNPERONIC A7	1	1	1
SYNPERONIC A3	3	3	3
Zeolite	24	24	24
Sokalan CP5	4	4	4
Sodium Carbonate	12	12	12
Sodium sulphate	18	18	18
Soluble "C" silicate	3	3	3
Sodium Chloride	4.68	4.68	4.68

In this case sodium chloride was included as being equivalent in ionic strength to 8% sodium perborate monohydrate.

In Examples 5 to 7 the nonionic surfactant mixture had an HLB of approximately 9.

The results were as follows:

Example No.	Anionic	Branched ?	% soil removal
5	ELFAN 280	No	27.8
6	SYNPROL SULPHATE	Yes	30.0
7	DOBANOL 45 SULPHATE	Yes	34.9

These results show that branched PAS outperforms the linear PAS.

Examples 8 to 11

Experiments using the method and compositions as used in Examples 6 and 7 were carried out at 30 ° C and 60 ° C on a different soiled polyester.

Example No.	Anionic	Temp °C	% Branching (4 and greater)	% Soil Removal
8	SYNPROL SULPHATE	30	2.3	44
9	DOBANOL 45 SULPHATE	30	8.8	48
10	SYNPROL SULPHATE	60	2.3	39.5
11	DOBANOL 45	60	8.8	49.5

These results show that a higher level of C_4 or greater branching in the PAS gives rise to a higher percentage of oily soil removal at both low and high temperatures.

Examples 12 to 13

Wash liquors were prepared in water having a hardness of 24 °FH to give a product concentration of 6g/l from a composition containing (by weight)

	12	13
SYNPROL SULPHATE (PAS)[1]	13	
ACROPOL SULPHATE (PAS)[2]		13
Zeolite	24	24
Sokalan CP5	4	4
Sodium carbonate	12	12
Sodium sulphate	10	10
Sodium metaborate	11	11

1 is C_{13}/C_{15} sulphate with 46% branching of which 78% is methyl and 5% is butyl or higher.
2 is a sulphate with 35% branching of which 50% is methyl and 21% is butyl or higher.

The wash liquors were used to wash a fabric load as in Example 1.
The results obtained were as follows.

Example No.	Anionic	% soil removal
12	SYNPROL SULPHATE	45.8
13	ACROPOL SULPHATE	49.1

From these results it is apparent that branched PAS with a high percentage of butyl branching outperforms PAS with a low percentage of butyl branching.

Examples 14 to 15

Examples 12 and 13 were repeated with nonionic detergent active in the formulation.

	14	15
SYNPROL SULPHATE (PAS)	6	-
ACROPOL SULPHATE (PAS)	-	6
SYNPERONIC A7	2	2
SYNPERONIC A3	6	6
ZEOLITE	24	24
SOKALAN CP5	4	4
SODIUM CARBONATE	12	12
SODIUM SULPHATE	10	10
SODIUM METABORATE	11	11

The results obtained were as follows.

Example No.	Anionic	% soil removal
14	SYNPROL SULPHATE	35.1
15	ACROPOL SULPHATE	38.0

Examples 16-18

Example 12 was repeated using three different PASs in place of SYNPROL SULPHATE. The results obtained were as follows:

Example No.	Anionic	% soil removal
16	C_{16} straight chain PAS	4.1 ± 0.8
17	C_{15}-2-methyl PAS	58.9 ± 2.3
18	C_{12}-2-butyl PAS	60.2 ± 2.5

These results show that branched PAS performs better than straight chain PAS.

Claims

1. A detergent composition for washing fabrics, the composition containing a surfactant system comprising an anionic surfactant the major ingredient of which is a primary alkyl sulphate having a primary alkyl chain length of between 10 and 20 carbon atoms, characterised in that more than 10% by weight of the total primary alkyl sulphate is branched, and more than 5% by weight of the total primary alkyl sulphate comprises material wherein the branches contain at least 4 carbon atoms.

2. A detergent composition as claimed in claim 1, characterised in that the surfactant system additionally comprises a nonionic surfactant.

3. A detergent composition as claimed in claim 2, characterised in that the nonionic surfactant has an HLB value of less than 10.5.

4. A detergent composition as claimed in any previous claim which comprises from 2 to 50% by weight of the surfactant system and from 15 to 60% by weight of a detergency builder.

Patentansprüche

1. Detergentzusammensetzung zum Waschen von Geweben, enthaltend ein Surfactant-System, umfassend ein anionisches Surfactant, dessen Hauptbestandteil ein primäres Alkylsulfat mit einer Kettenlänge des primären Alkyls von zwischen 10 und 20 Kohlenstoffatomen ist, **dadurch gekennzeichnet,** daß mehr als 10 Gewichtsprozent des gesamten primären Alkylsulfats verzweigt sind und mehr als 5 Gewichtsprozent des gesamten primären Alkylsulfats Material enthalten, in welchem die Verzweigungen zumindest 4 Kohlenstoffatome enthalten.

2. Detergentzusammensetzung nach Anspruch 1, **dadurch gekennzeichnet,** das Surfactant-System zusätzlich ein nichtionisches Surfactant enthält.

3. Detergentzusammensetzung nach Anspruch 2, **dadurch gekennzeichnet,** daß das nichtionische Surfactant einen HLB-Wert von kleiner als 10,5 aufweist.

4. Detergentzusammensetzung nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet,** daß sie von 2 bis 50 Gewichtsprozent des Surfactant-Systems und von 15 bis 60 Gewichtsprozent eines Waschkraftbuilders enthält.

Revendications

1. Composition détergente pour lavage d'articles textiles, la composition contenant un système tensioactif qui comprend un tensioactif anionique dont l'ingrédient principal est un alkylsulfate primaire ayant une longueur de chaîne alkylique primaire comprise entre 10 et 20 atomes de carbone, caractérisée en ce que plus de 10% en poids de l'alkylsulfate primaire total sont ramifiés et plus de 5% en poids de l'alkylsulfate primaire total comprennent une matière dont les ramifications renferment au moins 4 atomes de carbone.

2. Composition détergente selon la revendication 1, caractérisée en ce que le système tensioactif comprend en outre un tensioactif non ionique.

3. Composition détergente selon la revendication 2, caractérisée en ce que le tensioactif non ionique présente un indice d'amphipathie inférieur à 10,5.

4. Composition détergente selon l'une quelconque des revendications précédentes qui comprend de 2 à 50% en poids de système tensioactif et de 15 à 60% en poids d'un adjuvant de détergence.